Conversion of *N*-alkyldiisopropylamines into *N*,*N*-bis(5-chloro-3-oxo[1,2]dithiol-4-yl)amines

Susana Barriga,[a] Lidia S. Konstantinova,[b] Carlos F. Marcos,[a] Oleg A. Rakitin,[b] Charles W. Rees,[c] Tomás Torroba,[d] Andrew J. P. White[c] and David J. Williams[c]

[a] *Departamento de Química Orgánica, Facultad de Veterinaria, Universidad de Extremadura, 10071 Cáceres, Spain*
[b] *N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences, Leninsky Prospect, 47, 117913 Moscow, Russia*
[c] *Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY*
[d] *Departamento de Química, Facultad de Ciencias, Universidad de Burgos, 09001 Burgos, Spain*

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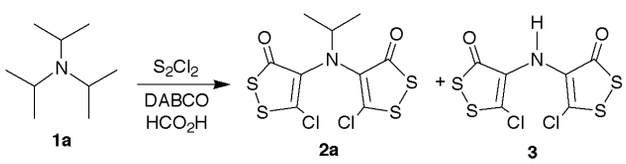
Triisopropylamine **1a** and S_2Cl_2, in the presence of DABCO and formic acid, give the bicyclic amine **2a**, and its *N*-dealkylated product **3**, rather than the tricyclic bisdithiolothiazine system **7** produced by Hünig's base **1b**. However, when S_2Cl_2 is in molar excess over DABCO, Hünig's base and related *N*-alkyldiisopropylamines **1c**–**g** also give the analogous bicyclic compounds **2b**–**g** together with the tricyclic compounds **7b**–**g**. The *N*-benzyl compound **2c** is debenzylated quantitatively to the secondary amine **3** by sulfuric acid. X-Ray crystallography of *N*,*N*-bis(dithiolyl)ethylamine **2b** shows the two dithiole rings to be steeply inclined to each other (85°) and the geometry at nitrogen to be slightly pyramidal. The crystal packing is dominated by S · · · O electrostatic and weak C=O · · · Cl charge-transfer interactions.

N-Ethyldiisopropylamine (Hünig's base) is a hindered non-nucleophilic base, commonly used as a deprotonating reagent in many organic reactions. In contrast to its generally assumed inertness, we have shown that it reacts with disulfur dichloride, S_2Cl_2, under very mild conditions to give bis[1,2]dithiolo[1,4]-thiazines,[1] bis[1,2]dithiolopyrroles,[2] and a dihydro[1,2]dithiolo-[1,4]thiazine,[3] in one-pot reactions. Under carefully controlled reaction conditions each of these heterocyclic systems can be obtained selectively.[4] Only the isopropyl groups react with S_2Cl_2, the ethyl group being inert. *N*-(2-Chloroethyl)diisopropyl-amine reacts similarly,[3] and even *N*-benzyldiisopropylamine reacts in the same way to give the *N*-benzyl bisdithiolo-thiazines and pyrroles and hence, by debenzylation, the parent *N*-H compounds.[5] To explore the limits of the reaction we have now included a third isopropyl group in the starting amine, subjecting the highly crowded triisopropylamine to the action of S_2Cl_2 and have obtained the first member of a new class of stable bis(1,2-dithiol-4-yl)amines. Furthermore we report how these bicyclic bis(dithiolyl)amines can be produced from other *N*-alkyldiisopropylamines in one-pot reactions with S_2Cl_2 under appropriate conditions.

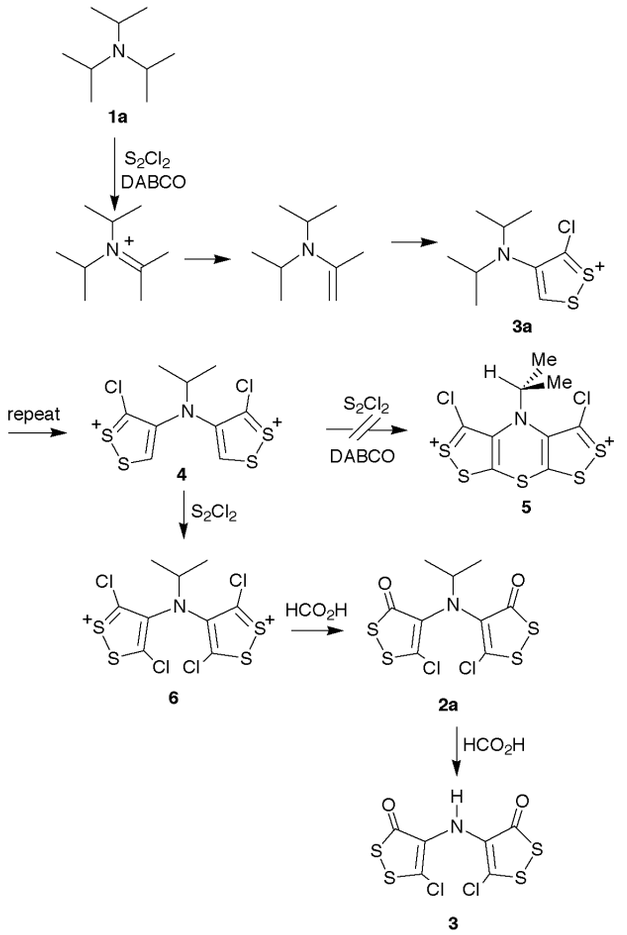
Triisopropylamine[6] **1a** was treated with S_2Cl_2 (15 equiv.) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (12 equiv.) in 1,2-dichloroethane for 3 d at room temperature. Formic acid (30 equiv.) was then added and the mixture heated under reflux for 1.5 h since this treatment gives cleaner reactions by facilitating the hydrolysis of intermediate 3-chlorodithiolium salts to dithiol-3-ones.[4] Products **2a**, orange solid, $C_9H_7Cl_2NO_2S_4$, mp 138–140 °C (12%) and **3**, orange solid, $C_6HCl_2NO_2S_4$, mp 144–145 °C (6%) were obtained after chromatography (Scheme 1). Structures **2a** and **3** were elucidated from mass spectrometry, HRMS, ^{1}H- and ^{13}C-NMR and IR spectroscopy. When triiso-propylamine **1a** was treated with an excess of S_2Cl_2 and DABCO in equimolecular proportions (16 equiv.), followed by treatment with formic acid, only **3** was isolated, in very small amounts; without the formic acid treatment no pure products



Scheme 1

could be isolated. It appears that for this amine an excess of S_2Cl_2 over DABCO is needed to furnish stable products. Under these conditions triisopropylamine starts to react like Hünig's base,[4] following the sequence of dehydrogenation, displacement of chlorine from S_2Cl_2 and chlorination, up to formation of the intermediate **4** (*cf.* ref. 4) (Scheme 2). The next step in our proposed mechanism would be cyclization of **4** to **5**,[4] but if we assume that these tricyclic dithiolium salts are highly delocal-ised and hence near-planar, the *N*-isopropyl intermediate **5** will be markedly more crowded than the *N*-ethyl analogue. Computational modelling[7] shows that the planar structure **5** is sterically forbidden. Instead of ring closure to **5**, **4** could be chlorinated further by the excess of S_2Cl_2 to give **6** which would be converted by formic acid into the bicyclic *N*-isopropyl com-pound **2a** which, in turn, could be slowly dealkylated by the hot acid to give the secondary amine **3** (Scheme 2). Interestingly, there was no sign that the remaining isopropyl group in **2a** had reacted with S_2Cl_2 to give a third 1,2-dithiole ring. This could be a consequence of the electron-withdrawing effect of the two dichlorodithiolium rings (or the derived chlorodithiolone rings) which would suppress the oxidation of the third *N*-isopropyl group to the iminium ion (*cf.* Scheme 2). For the same reason one *N*-acetyl or *N*-cyano group protects diisopropylamine from reaction with S_2Cl_2 under the same conditions.[4]

We have proposed in Scheme 2 that bis-dithiolium salt **4** is the key intermediate which is diverted from further cyclisation by ring chlorination when DABCO is in deficiency with respect



Scheme 2

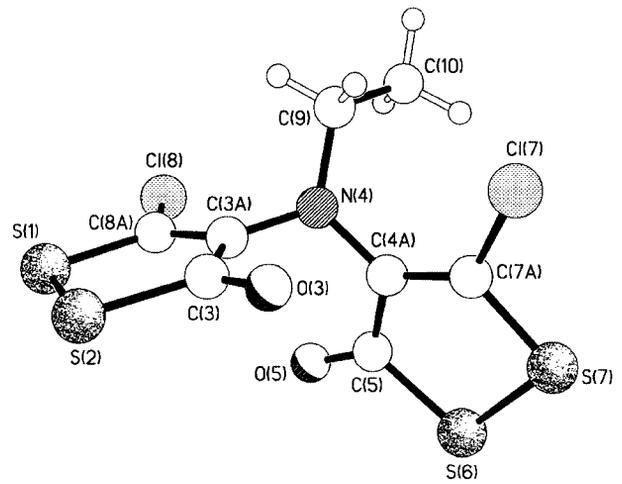
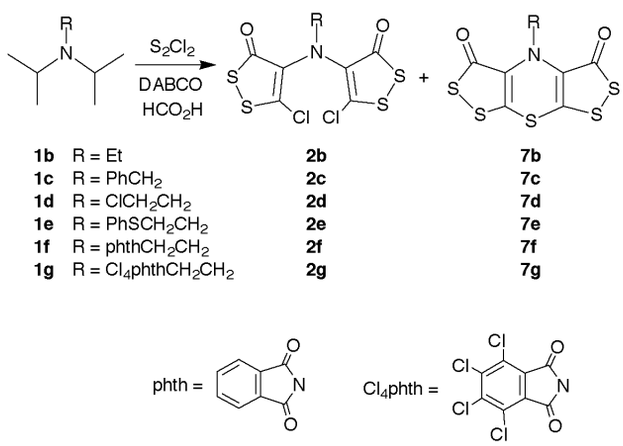


Fig. 1 The molecular structure of **2b**. Selected bond lengths (Å) are: S(1)–C(8A) 1.735(4), S(1)–S(2) 2.050(2), S(2)–C(3) 1.792(4), C(3)–O(3) 1.208(5), C(3)–C(3A) 1.456(6), C(3A)–C(8A) 1.347(6), C(3A)–N(4) 1.408(5), N(4)–C(4A) 1.405(5), N(4)–C(9) 1.472(5), C(4A)–C(7A) 1.347(6), C(4A)–C(5) 1.468(5), C(5)–O(5) 1.204(5), C(5)–S(6) 1.787(4), S(6)–S(7) 2.046(2), S(7)–C(7A) 1.727(4), C(7A)–Cl(7) 1.706(4), C(8A)–Cl(8) 1.701(4).



1b	R = Et	**2b**	**7b**
1c	R = $PhCH_2$	**2c**	**7c**
1d	R = $ClCH_2CH_2$	**2d**	**7d**
1e	R = $PhSCH_2CH_2$	**2e**	**7e**
1f	R = $phthCH_2CH_2$	**2f**	**7f**
1g	R = $Cl_4phthCH_2CH_2$	**2g**	**7g**

Scheme 3

to disulfur dichloride. If this assumption is correct a similar diversion of the reaction of other *N*-alkyldiisopropylamines might also be observed under the same conditions to give hitherto undetected bicyclic products analogous to **2a**, and we now find this to be the case. Thus, *N*-ethyldiisopropylamine **1b** (1 equiv.) was treated with S_2Cl_2 (10 equiv.) and DABCO (6 equiv.) in 1,2-dichloroethane for 3 d at room temperature. Formic acid (20 equiv.) was then added and the mixture heated under reflux for 1.5 h. Chromatography afforded the bicyclic product **2b**, yellow solid, $C_8H_5Cl_2NO_2S_4$, mp 132–133 °C (19%) and the previously reported tricyclic product **7b**[4] (10%) (Scheme 3). The structure of **2b** was determined from mass spectrometry, HRMS, ^{1}H- and ^{13}C-NMR and IR spectroscopy and was confirmed by X-ray diffraction (see below). Analogous treatment of *N*-benzyldiisopropylamine **1c** with S_2Cl_2 (10 equiv.) and DABCO (6 equiv.) in 1,2-dichloroethane for 3 d at room temperature followed by addition of formic acid (20 equiv.) and heating under reflux for 1 h gave **2c**, yellow crystals, mp 164–165 °C (15%) in addition to the previously reported compound **7c**[5] (27%) (Scheme 3). The structure of **2c** was fully supported by its spectroscopic properties. Treatment of a dilute solution of the *N*-benzyl compound **2c** in dichloromethane with concentrated sulfuric acid at 5–10 °C for 30 min gave a quantitative yield of the debenzylated compound **3**, identical with that from triisopropylamine **1a**.

Similarly, treatment of *N*-(2-chloroethyl)diisopropylamine **1d** with S_2Cl_2, DABCO and formic acid (20 equiv.) as shown in Table 1 gave the bicyclic compound **2d**, yellow crystals, $C_8H_4Cl_3NO_2S_4$, mp 97–98 °C (7%) in addition to tricyclic compound **7d**[3] (20%). In the same way the *N*-phenylthioethyl **1e**, phthalimidoethyl **1f**, and tetrachlorophthalimidoethyl **1g** derivatives of diisopropylamine, which were prepared from **1d**,[8] were converted into the analogous bicyclic (*ca.* 20% yield) and tricyclic (*ca.* 15% yield) compounds (Scheme 3 and Table 1). These results are all explicable by the mechanism proposed in Scheme 2 where the bisdithiolium intermediate (*cf.* **4**) is either chlorinated further or (except for *N*-isopropyl) cyclised to a 1,4-thiazine.

The complex reactions of *N*-alkyldiisopropylamines with S_2Cl_2 provide new routes to novel heterocyclic structures by diversion of intermediates on the way to complete sulfuration of both isopropyl groups. We have now shown that chlorination by S_2Cl_2 and a deficiency of DABCO, and hydrolysis by formic acid, of these readily available tertiary amines give *N*,*N*-bis(1,2-dithiol-4-yl)amine **3** and its *N*-alkyl derivatives **2b**–**g** in one-pot, though low-yielding, reactions. Whilst 5-amino derivatives of 1,2-dithiol-3-ones and -thiones are readily available by displacement of chlorine from the activated 5-position,[9] 4-amino isomers like **2** and **3** appear to be very rare.[10]

The X-ray analysis of **2b** confirmed the bisdithiole nature of the compound (Fig. 1), the two dithiole rings being inclined almost orthogonally (85° between their mean planes), this geometric arrangement being produced by torsional twists of 59 and 61° about the C(3A)–N(4) and N(4)–C(4A) bonds respectively. The geometry at the nitrogen centre is slightly pyramidalized with N(4) lying 0.16 Å out of the C(3A)–C(4A)–C(9) plane—the dithiole rings are inclined by 69 [C(3A)] and 50° [C(4A)] to this plane. The pattern of bonding within each ring reflects the formal double bond character of the C(3A)–C(8A)

Table 1 Reaction of amines with S_2Cl_2, DABCO and formic acid

Amine	Reagents: Amine/ mmol	S_2Cl_2/ mmol	DABCO/ mmol	Formic acid/ mmol	Reflux time/min	Yields of products (%)			
1a	5	75	60	150	90	**2a**	12	**3**	6
1b	5	50	30	100	60	**2b**	19	**7b**[4]	10
1c	5	50	30	100	60	**2c**	15	**7c**[5]	20
1d	5	50	25	100	45	**2d**	7	**7d**[3]	20
1e[a]	5	50	30	100	45	**2e**	15	**7e**[7]	17
1f	5	50	25	100	60	**2f**	20	**7f**[7]	15
1g[a]	5	50	25	100	45	**2g**	22	**7g**[7]	16

[a] Tetramethylammonium chloride (30 mg) was added to the reaction mixture.

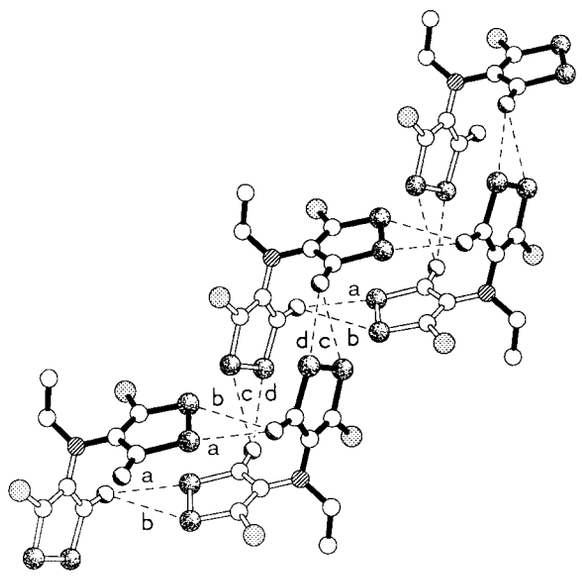


Fig. 2 Part of one of the loosely-linked chains of molecules present in the crystals of **2b**. The intrachain S···O contacts are: a) 3.12, b) 3.06, c) 3.08 and d) 3.08 Å.

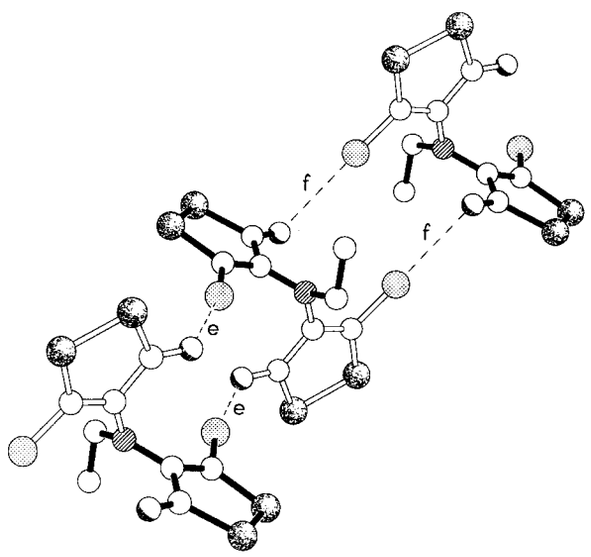
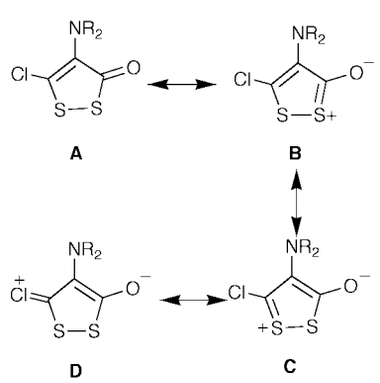


Fig. 3 The C=O···Cl linking of adjacent centrosymmetrically related chains. The O···Cl distances are: e) 3.03 and f) 3.04 Å.



Scheme 4

and C(4A)–C(7A) linkages [both 1.347(6) Å], though these distances are noticeably greater than that for an isolated C=C and indicate a degree of delocalisation within the ring system. Structural data for 1,2-dithiol-3-one ring systems are sparse and, with the exception of the fused ring systems that we have described previously,[4,5] the current release of the Cambridge Crystallographic Database (October 1998) contains only two other examples[11,12] of pendant 1,2-dithiol-3-one containing systems. Of these, the closer analogue is 4-methyl-5-(pyrazin-2-yl)-3*H*-1,2-dithiol-3-one where the pattern of bonding in the dithiole ring does not differ significantly from that observed here.

The packing of the molecules (Fig. 2) is dominated by electrostatic O···S interactions (ranging between 3.06 and 3.12 Å) and parallel stacking of the dithiole rings of symmetry related molecules; the mean interplanar separations are 3.73 [C(3A) ring to C(3A) ring] and 3.85 Å [C(4A) ring to C(4A) ring]. These interactions combine to form rather elegant twisted chains that extend in the crystallographic *c* direction. Adjacent C_i-related chains are oriented such that the carbonyl groups in one chain are directed towards the chlorine atoms in the next and *vice versa* (Fig. 3). The O···Cl distances, 3.03 and 3.04 Å, are significantly less than the sum of their van der Waals radii (*ca.* 3.2 Å) and clearly indicate some form of intermolecular interaction. If we ignore the possibility of significant intramolecular electron-transfer between the two dithiole rings, then the 4-amino-5-chloro-1,2-dithiole moiety can be represented by the resonance forms **A**–**C** in Scheme 4, with a minor contribution from **D**. The oxygen atom carries a partial negative charge, explaining the 3-centre O···S interactions a to d in Fig. 2, which are clearly electrostatic. If a small positive charge were induced on the chlorine atom, as in contribution **D**, then the intermolecular O···Cl interactions e and f (Fig. 3) could also be electrostatic in nature, but the observed bond lengths do not indicate any marked shortening of either the C–Cl or the C(3A)–C(3) [C(4A)–C(5)] bond lengths. A survey of the literature reveals that short intermolecular C=O···Cl contacts are relatively commonplace (159 examples in the range 2.86–3.20 Å), though infrequently commented upon. However, two particular examples, in the structure of 2,3-dichlorobenzo-1,4-quinone,[13] and perhaps more relevantly in that of 5-chloropyrimidin-2-one,[14] this type of interaction has been attributed to "donor–acceptor" and "charge transfer" bonding

respectively. Examples of strong interactions of this type have been discussed in a review by Hassel and Rømming[15] and are considered to involve a lone pair on the carbonyl and the d-orbitals of the halogen. We think it likely that the C=O···Cl contacts in the structure of **2b** are probably examples of weak interactions of this type.

Experimental

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Bruker Vector 200 A instrument in KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 400 in $CDCl_3$ or d_5-pyridine solution. CH groups were distinguished by DEPT experiments. *J* values are given in Hz. Mass spectra were recorded on VG7070E and VG-AutoSpec instruments using electron impact ionisation. Light petroleum refers to the fraction bp 40–60 °C.

General procedure for the preparation of *N*,*N*-bis(5-chloro-3-oxo-1,2-dithiol-4-yl)alkylamines 2a–g

Disulfur dichloride was added dropwise to a stirred solution of *N*-alkyldiisopropylamine **1a**–**g** and DABCO dissolved in 1,2-dichloroethane (150 ml) at −40 °C. The mixture was stirred for 15 min at −40 °C, then for 3 days at room temperature. Formic acid was then added dropwise at 5 °C and the mixture was refluxed for 45 min to 1.5 h. The reaction mixture was filtered through Celite and the solvent was removed in a rotary evaporator. Medium pressure liquid chromatography (MPLC) (silica gel Merck 60, light petroleum to CH_2Cl_2) of the residue afforded products **2a**–**g**, in addition to the previously reported products **7b**–**g**. The reaction conditions and yields of products are given in Table 1.

***N*,*N*-Bis(5-chloro-3-oxo-1,2-dithiol-4-yl)isopropylamine 2a.** Orange solid (from light petroleum–CH_2Cl_2), mp 138–140 °C (Found M^+, 358.8734. $C_9H_7Cl_2NO_2S_4$ requires *M*, 358.8737) (Found: C, 30.25; H, 2.0; N, 3.8. $C_9H_7Cl_2NO_2S_4$ requires C, 30.0; H, 2.0; N, 3.9%); δ_H ($CDCl_3$) 4.34 (heptet, 1H, *J* 7.0, CH), 1.21 (d, 6H, *J* 7.0, 2 × CH_3); δ_C ($CDCl_3$) 187.02 (C=O), 150.52 and 133.86 (2 × sp^2 tertiary C), 51.40 (CH), 21.45 (CH_3); ν_{max}/cm^{-1} 2978, 2929, 1646 (C=O), 1524, 1382, 1260, 1123, 805, 714, 620; *m*/*z* 363 (M^+ + 4, 16%), 361 (M^+ + 2, 58), 359 (M^+, 68), 344 (M − CH_3, 32), 323 (M − HCl, 74), 317 (M − C_3H_6, 29), 256 (M − C_3H_7SCO, 77), 225 ($C_5HCl_2NOS_2$, 37), 79 ($ClCS^+$, 94), 43 ($C_3H_7^+$, 100).

***N*,*N*-Bis(5-chloro-3-oxo-1,2-dithiol-4-yl)amine 3.** Orange solid (from light petroleum–CH_2Cl_2), mp 144–145 °C (Found M^+, 316.8201. $C_6HCl_2NO_2S_4$ requires *M*, 316.8267) (Found: C, 22.8; H, 0.35; N, 4.35. $C_6HCl_2NO_2S_4$ requires C, 22.65; H, 0.3; N, 4.4%); δ_H ($CDCl_3$) 5.54 (br s, 1H, NH); δ_C ($CDCl_3$) 185.52 (C=O), 139.65 and 129.36 (2 × sp^2 tertiary C); ν_{max}/cm^{-1} 3302 (N–H), 1614 (C=O), 1575, 1550, 1453, 1283, 1094, 563; *m*/*z* 321 (M^+ + 4, 24%), 319 (M^+ + 2, 84), 317 (M^+, 100), 256 (M − HSCO, 35) (Found M^+, 255.8517. $C_5Cl_2NO_2S_3$ requires *M*, 255.8519), 225 (M − COS_2, 16) (Found M^+, 224.8854. $C_5HCl_2NO_2S_2$ requires *M*, 224.8877), 218 (M − $CHCl_2O$, 17) (Found M^+, 217.8866. C_5NOS_4 requires *M*, 217.8863), 210 (M- C_2ClOS, 20) (Found M^+, 209.8909. $C_4HClNOS_3$ requires *M*, 209.8909), 79 ($ClCS^+$, 47) (Found M^+, 78.9407. CClS requires *M*, 209.8909).

***N*,*N*-Bis(5-chloro-3-oxo-1,2-dithiol-4-yl)ethylamine 2b.** Yellow solid (from light petroleum–CH_2Cl_2), mp 132-133 °C (Found M^+, 344.8579. $C_8H_5Cl_2NO_2S_4$ requires *M*, 344.8502) (Found: C, 27.9; H, 1.5; N, 4.0. $C_8H_5Cl_2NO_2S_4$ requires C, 27.75; H, 1.5; N, 4.0%); δ_H ($CDCl_3$) 3.70 (q, 2H, *J* 7.1, CH_2), 1.18 (t, 3H, *J* 7.1, CH_3); δ_C ($CDCl_3$) 185.99 (C=O), 146.54 and 133.52 (2 × sp^2 tertiary C), 44.58 (CH_2, from DEPT), 14.77 (CH_3, from DEPT); ν_{max}/cm^{-1} 2981, 2931, 2875, 1634 (C=O), 1535, 1252, 1122, 1047, 612; *m*/*z* 349 (M^+ + 4, 6%), 347(M^+ + 2, 22), 345 (M^+, 25), 309 (M − HCl, 9), 274 (M − HCl_2, 8), 218 (M − $C_3H_5Cl_2O$, 11), 210 (M − C_4H_4ClOS, 10), 79 ($ClCS^+$, 94). *Crystal data for* **2b**: $C_8H_5Cl_2NO_2S_4$, *M* = 346.3, triclinic, $P\bar{1}$ (no. 2), *a* = 7.814(2), *b* = 8.211(1), *c* = 10.115(2) Å, *α* = 86.50(1), *β* = 88.77(2), *γ* = 85.46(1)°, *V* = 645.6(2) Å^3, *Z* = 2, D_c = 1.781 g cm^{-3}, *μ*(Cu-K*α*) = 104.9 cm^{-1}, *F*(000) = 348, *T* = 293 K; yellow rhombs, 0.43 × 0.27 × 0.21 mm, Siemens P4/PC diffractometer, *ω*-scans, 2088 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically using full matrix least-squares based on F^2 to give R_1 = 0.047, wR_2 = 0.128 for 1784 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 126°$] and 155 parameters.†.

***N*,*N*-Bis(5-chloro-3-oxo-1,2-dithiol-4-yl)benzylamine 2c.** Orange solid (from light petroleum–CH_2Cl_2), mp 164–165 °C (Found M^+, 406.8743. $C_{13}H_7Cl_2NO_2S_4$ requires *M*, 406.8737) (Found: C, 38.4; H, 1.8; N, 3.5. $C_{13}H_7Cl_2NO_2S_4$ requires C, 38.2; H, 1.7; N, 3.4%); δ_H (d_5-pyridine) 7.76 (d, *J* 7.3, 2H, ArH), 7.31 (t, *J* 7.7, 2H, ArH), 7.21 (t, *J* 7.4, 1H, ArH), 5.05 (s, 2H, CH_2); δ_C (d_5-pyridine) 187.26 (C=O), 148.07, 137.35 and 134.40 (3 × sp^2 tertiary C), 129.36, 128.74 and 128.28 (3 × ArH, from DEPT), 53.06 (CH_2, from DEPT); ν_{max}/cm^{-1} 3053, 2934, 1658 (C=O), 1541, 1453, 1381, 1069, 955, 694, 560; *m*/*z* 411 (M^+ + 4, 1%), 409 (M^+ + 2, 6), 407 (M^+, 6), 371 (M − HCl, 2), 91 ($C_7H_7^+$, 100).

***N*,*N*-Bis(5-chloro-3-oxo-1,2-dithiol-4-yl)(2-chloroethyl)amine 2d.** Yellow crystals (from light petroleum–CH_2Cl_2), mp 97–98 °C (Found M^+, 378.8180. $C_8H_4Cl_3NO_2S_4$ requires *M*, 378.8190) (Found: C, 25.5; H, 1.15; N, 3.5. $C_8H_4Cl_3NO_2S_4$ requires C, 25.2; H, 1.1; N, 3.7%); δ_H ($CDCl_3$) 3.93 (t, *J* 6.8, 2H, CH_2), 3.75 (t, *J* 6.8, 3H, CH_2); δ_C ($CDCl_3$) 186.16 (C=O), 147.57 and 133.35 (2 × sp^2 tertiary C), 50.63 and 42.97 (2 × CH_2, from DEPT); ν_{max}/cm^{-1} 2964, 1627 (C=O), 1547, 1533, 1078, 1007, 821; *m*/*z* 383 (M^+ + 4, 7%), 381 (M^+ + 2, 15), 379 (M^+, 14), 347 (M^+ + 4 − HCl, 16), 345 (M^+ + 2 − HCl, 16), 343 (M^+ − HCl, 62), 308 (M^+ − HCl_2, 14), 160 ($C_5H_3ClNOS^+$, 45), 79 ($ClCS^+$, 100).

***N*,*N*-Bis(5-chloro-3-oxo-1,2-dithiol-4-yl)(2-phenylthioethyl)-amine 2e.** Yellow solid (from light petroleum–CH_2Cl_2), mp 81–83 °C (Found M^+, 452.8631. $C_{14}H_9Cl_2NO_2S_5$ requires *M*, 452.8614) (Found: C, 37.2; H, 2.1; N, 3.0. $C_{14}H_9Cl_2NO_2S_5$ requires C, 37.0; H, 2.0; N, 3.1%); δ_H ($CDCl_3$) 7.35 (dt, J_{ab} 8.0, $J_{ac/ad}$ 1.5, 2H, Ph_{ortho}), 7.27 (td, J_{ba} 8.0, J_{be} 2.3, 2H, Ph_{meta}), 7.18 (tt, J_{cb} 7.3, J_{ca} 1.9, 1H Ph_{para}), 3.81 (t, *J* 7.9, 2H, CH_2), 3.17 (t, *J* 7.9, 2H, CH_2); δ_C ($CDCl_3$) 185.99 (C=O), 147.12, 135.20 and 133.31 (3 × sp^2 tertiary C), 129.47, 128.97 and 126.34 (3 × CH_{aromat}, from DEPT), 49.19 and 32.98 (2 × CH_2, from DEPT); ν_{max}/cm^{-1} 3042, 3008, 2977, 2935, 1655 (C=O), 1582, 1542, 1478, 1441, 1069, 802, 740, 690; *m*/*z* 453 (M^+, 1%), 346 (M^+ + 2 − C_6H_5S, 26), 344 (M^+ − C_6H_5S, 34), 79 ($ClCS^+$, 95), 77 ($C_6H_5^+$, 100).

***N*,*N*-Bis(5-chloro-3-oxo-1,2-dithiol-4-yl)(2-phthalimidoethyl)-amine 2f.** Orange solid (from light petroleum–CH_2Cl_2), mp 162–163 °C (Found M^+, 489.8747. $C_{16}H_8Cl_2N_2O_4S_4$ requires *M*, 489.8744) (Found: C, 39.3; H, 1.7; N, 5.6. $C_{16}H_8Cl_2N_2O_4S_4$ requires C, 39.1; H, 1.6; N, 5.7%); δ_H ($CDCl_3$) 7.83 (dd, J_{ab} 5.4, J_{ac} 3.1, 2H, $PhthH_{ortho}$), 7.70 (dd, J_{ba} 5.4, J_{bd} 3.1, 2H, $PhthH_{meta}$), 4.14 (t, *J* 5.9, 2H, CH_2), 3.91 (t, *J* 5.9, 2H, CH_2); δ_C ($CDCl_3$) 187.01 (C=O), 168.42 (N–C=O), 155.19, 146.56 and 145.31 (3 × sp^2 tertiary C), 134.36 and 123.72 (2 × CH_{aromat}),

† CCDC reference number 207/348. See http://www.rsc.org/suppdata/p1/1999/2237 for crystallographic files in .cif format.

47.61 and 37.21 (2 × CH_2); ν_{max}/cm^{-1} 1772 and 1720 (N–C=O), 1655 and 1638 (C=O), 1394, 1289, 1044; *m*/*z* 494 (M^+ + 4, 5%), 492 (M^+ + 2, 17), 490 (M^+, 20), 347 (M^+ + 4 − phthH, 10), 345 (M^+ + 2 − phthH, 35), 343 (M^+ − phthH, 46), 334 (M^+ + 4 − phthCH_2, 7), 332 (M^+ + 2 − phthCH_2, 24), 330 (M^+ − phthCH_2, 29), 308 (M^+ − phthHCl, 11), 174 (phth-$C_2H_4^+$, 68), 160 (phthCH_2^+, 76), 147 (phthH^+, 37), 130 (phth$^+$ − O, 100).

***N*,*N*-Bis(5-chloro-3-oxo-1,2-dithiol-4-yl)[2-(tetrachlorophthalimido)ethyl]amine 2g.** Orange solid (from light petroleum–CH_2Cl_2), mp 244–245 °C (Found M^+, 627.7106. $C_{16}H_4Cl_5{}^{37}ClN_2O_4S_4$ requires *M*, 627.7156) (Found: C, 27.9; H, 1.0; N, 3.4. $C_{16}H_4Cl_6N_2O_4S_4 \cdot 2CH_2Cl_2$ requires C, 27.1, H, 1.0, N 3.5%); δ_H 4.0 (dd, J_a 7.0, J_b 5.0, 2H, CH_2), 3.82 (dd, J_a 7.0, J_b 5.0, 2H, CH_2); δ_C 186.35 (C=O), 163.39 (N–C=O), 147.91, 139.80, 132.97, 130.38 and 129.49 (5 × sp^2 tertiary C), 46.82 and 36.82 (2 × CH_2); ν_{max}/cm^{-1} 2933, 1779 and 1720 (N–C=O), 1666 and 1627 (C=O), 1548, 1534, 1397, 1355, 1070, 743; *m*/*z* 638 (M^+ + 8, 5%), 632 (M^+ + 6, 15), 630 (M^+ + 4, 14), 629 (M^+ + 2 + H, 21), 628 (M^+ + 2, 35), 626 (M^+, 16), 347 (M^+ + 4 − Cl_4phthH, 25), 345 (M^+ + 2 − Cl_4phthH, 83), 343 (M^+ − Cl_4phthH, 100), 334 (M^+ + 4 − Cl_4phthCH_2, 17), 332 (M^+ + 2 − Cl_4phthCH_2, 58), 330 (M^+ − Cl_4phthCH_2, 71), 310 (M^+ − Cl_4phthSH, 27), 296 (Cl_4phthCH_2^+, 20), 266 (Cl_4phth$^+$ − O, 38), 79 ($ClCS^+$, 100).

***N*,*N*-Bis(5-chloro-3-oxo-1,2-dithiol-4-yl)amine 3 by debenzylation.** *N*,*N*-Bis(5-chloro-3-oxo-1,2-dithiol-4-yl)benzylamine **2c** (110 mg, 0.27 mmol) was treated with concentrated sulfuric acid (0.6 ml) in dichloromethane (40 ml) at 5–10 °C for 30 min, then water (50 ml) was added and the organic layer separated, washed and dried ($MgSO_4$), affording *N*,*N*-bis(5-chloro-3-oxo-1,2-dithiol-4-yl)amine **3** (85 mg, 99%) identical with that described above.

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